

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant	:	VEHKAMAKI et al.
Filed	:	October 28, 2003
For	:	PROCESS FOR PRODUCING OXIDE FILMS
Examiner	:	Kelly M. Gambetta
Group Art Unit	:	1792

**DECLARATION OF SUVI HAUKKA UNDER 37 C.F.R. § 1.132**

**Mail Stop AF**  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I, Suvi Haukka, do hereby declare and say as follows:

1. I am currently employed as an Executive Scientist for ALD applications for ASM Microchemistry Oy, in Helsinki, Finland. For the past nineteen years I have worked in various capacities including Research Scientist, Catalyst Technology Manager, Process Development Manager and R&D Manager which all have been related to atomic layer deposition (ALD). In particular, my work has focused on ALD and applications of it for semiconductor equipment, processes, and devices as well as development of ALD apparatus. Over the course of my career, I have been an author on over 60 scientific papers, primarily concerning ALD processes, applications and apparatus. In addition, I am an inventor of more than 60 patents and patent applications in the field of semiconductor fabrication. In 1994 I earned a Doctor of Philosophy degree from Laboratory of Analytical Chemistry, University of Helsinki, Finland.

2. I have read and understand the claims in the present patent application. I understand that the claims generally concern processes for producing bismuth oxide films or

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layers by Atomic Layer Deposition (ALD) using an organic bismuth compound as a source material and depositing the bismuth oxide at a temperature of less than about 250°C.

3. I am familiar with the course of prosecution of the present patent application, including the Office Action mailed December 12, 2008, in which Gordon et al. (WO02/27063) and Hintermaier et al. (U.S. Patent No. 6,177,135) were discussed. I understand that the Examiner concluded that the skilled artisan would understand Gordon et al., and Gordon et al. in view of Hintermaier et al., to render obvious ALD processes for producing bismuth oxides as claimed. For the reasons detailed below, I disagree with this conclusion.

4. As an expert in the field of semiconductor fabrication, I had an understanding of the scientific and engineering principles applicable to equipment and processes for thin film deposition, particularly for CVD and ALD, at the time the present application was filed.

5. As shown on page 16 of Gordon et al., Table 1 lists compounds that are "volatile." It is my understanding that most volatile compounds can, in principle, be used for CVD. However, it is my opinion, and the ordinary engineer would understand, that volatility of a compound is not sufficient to indicate that it can be used in ALD. Unlike CVD, ALD depends on specific surface reactions. As a result, a compound must meet more criteria to be suitable for ALD. Specifically, there are at least five criteria that should be met for a material to be useful as a precursor for ALD: 1) the compound should be volatile or capable of being evaporated; 2) the compound should be in a vapor phase without decomposing; 3) the compound should be capable of reacting with the surface of a substrate without decomposing at the deposition temperature; 4) the evaporated compound should bind to the surface chemically (e.g., by "chemisorption") when contacted with the surface of a substrate; and 5) the compound should bind to the surface of the substrate through at least one ligand, while the other ligands remain intact to provide for saturation of the surface (e.g., in "self-limiting reactions").

6. Further regarding the fifth requirement above, if the ligands of a precursor molecule were cleaved off (e.g., when decomposed) when it reacts with the surface of a substrate, new binding sites on the bound molecule could form that are capable of reacting

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further with other molecules, and the reaction would not be self-limiting. Thus, if a precursor molecule is decomposed or its ligands cleaved off, no new sites must be formed on the molecule in order for the growth to be limited to about one molecular layer per ALD cycle. The ordinary engineer would understand that the self limiting surface reactions are an essential characteristic of ALD.

7. As an illustration of all the above criteria, the following description of forming aluminum oxide by ALD from aluminum precursor  $Al_2(CH_3)_3$  (e.g., "TMA") and water is described here, and on page 2 of the attached publication "Atomic Layer Chemical Vapor Deposition of High-k Gate Dielectrics," which I have co-authored. TMA is introduced in an inert gas flow to a substrate that has OH groups (such as Si-OH on  $SiO_2$ ) on the surface. Chemical bonds are formed between TMA and the surface of the substrate, and the reaction is continued until all the available reactive sites have reacted. After the TMA has reacted and all the available Si-OH groups have been occupied, the surface will be terminated with  $-CH_3$  groups. The reaction conditions are self-limiting because the  $-CH_3$  groups cannot serve as reactive sites for TMA, and the reactions will automatically stop. After the surface has become 'saturated' and all reactions ended, the system is purged with an inert gas to remove the surplus of gaseous TMA and  $CH_4$  molecules. A second reactant, e.g. water, is then introduced to remove the intact ligands and convert them to further OH groups that are capable of reacting with the TMA molecules of the subsequent reactant pulse.

8. I understand that the Examiner alleges that Gordon et al. teaches "CVD or ALD" and that the Examiner understands this disclosure to "broadly teach" the claimed ALD processes using the claimed bismuth precursor. (See Final Office Action, page 2). I disagree. I also disagree with the Examiner's allegation that Gordon et al. teaches ALD and CVD "using the same precursors for both ALD and CVD." (*Id.*). In view of the above, it is clear that the ordinary engineer would not know whether a compound that may be used for CVD can meet all the above kinetic criteria to be suitable for ALD, merely from the chemical name, structure or the melting point of the compound, for example, as listed in Gordon et al. It is also my understanding that a majority of the compounds listed in Table 1 of Gordon et al. has not been tested for use in ALD. It is my opinion that it is not possible to know which of the compounds

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listed in Table 1 could be suitable for ALD based on the disclosure of Gordon et al. Thus, it is my opinion that the ordinary engineer would not presume that any particular compound, such as any of those listed in Gordon et al., would automatically be suitable for use in ALD.

9. It is also my opinion that many, if not most, of the compounds listed in Table 1 would not work in ALD, because many of the listed compounds have insufficient vapor pressure, and some of the listed compounds decompose when evaporated (e.g.,  $\text{Cu}_4(\text{N}(\text{SiMe}_3)_2)_4$ ). Thus, it is further my opinion that many of the compounds listed in Table 1 are not suitable for use in ALD with industrially feasible growth rates. For example, lanthanum silylamides, such as  $\text{La}(\text{N}(\text{SiMe}_3)_2)_3$ ,  $\text{La}(\text{N}^t\text{BuSiMe}_3)_3$  and  $\text{La}(\text{N}^i\text{Pr}_2)_3$  in table 1 and  $\text{LaCp}_3$  in table 2 are too unstable to be used as ALD precursor as also referred to in Haukka, S., ECS Transactions 3 (15) 15-26 (2007) pp 20.

10. The provision of a CVD precursor without other reactive gases is not “analogous” to the first step of ALD, as the Examiner alleges on pages 2-3 of the Office Action. Specifically, CVD requires decomposition of precursors but, as noted above, precursors for ALD must meet a number of criteria, including being capable of reacting with the surface of a substrate without decomposition. Thus, the provision of a given CVD precursor (such as those disclosed in Table 1 of Gordon et al., Hintermaier et al., or elsewhere) without other reactive gases is not “analogous” to the first step of ALD because the reaction of the CVD precursor with the surface of a substrate would not necessarily be self-limiting in the specific ways that are essential to ALD processes as described above.

11. For the reasons presented above, CVD precursors cannot simply be substituted into ALD reactions and expected to work. There is no reason to believe that any of the precursors in Table 1 of Gordon et al. would be suitable for ALD reactions. Thus, the ordinary engineer would not have had any reason to deposit bismuth oxide films by ALD using an organic bismuth compound as a source material, based on the teachings of Gordon et al.

12. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I declare that these statements were made with the knowledge that willful false statements and the like so

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made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: June 11, 2009

By: Suvi Haukka

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